CA20N EV665 1990 P315 c.2

PHYTOTOXICOLOGY ASSESSMENT
SURVEY INVESTIGATION
IN THE VICINITY OF
ALLIED CHEMICAL CANADA LIMITED
AND
GENERAL CHEMICAL CANADA LIMITED
AMHERSTBURG, ONTARIO – 1987

JULY 1990



Copyright Provisions and Restrictions on Copying:

This Ontario Ministry of the Environment work is protected by Crown copyright (unless otherwise indicated), which is held by the Queen's Printer for Ontario. It may be reproduced for non-commercial purposes if credit is given and Crown copyright is acknowledged.

It may not be reproduced, in all or in part, for any commercial purpose except under a licence from the Queen's Printer for Ontario.

For information on reproducing Government of Ontario works, please contact ServiceOntario Publications at copyright@ontario.ca

EN 665

ISBN 0-7729-5413-5

PHYTOTOXICOLOGY ASSESSMENT SURVEY INVESTIGATION '

IN THE VICINITY OF

ALLIED CHEMICAL CANADA LIMITED

AND

GENERAL CHEMICAL CANADA LIMITED

AMHERSTBURG, ONTARIO - 1987

Report prepared by:
William I. Gizyn
Phytotoxicology Section
Air Resources Branch
Ontario Ministry of the Environment

ARB 186-88-PHYTO

JULY 1990



Copyright: Queen's Printer for Ontario, 1990
This publication may be reproduced for non-commercial purposes with appropriate attribution

LOG# 88-2231-186

Table of Contents

1	Executive Summary	1
2	Introduction 2.1 Industrial Sources 2.2 Phytotoxicology Section Surveys 2.3 Control Orders	2 3
3	1987 Phytotoxicology Vegetation Survey 3.1 Sampling Stations and Dates 3.2 Prevailing Winds 3.3 Foliage Sampling and Processing 3.4 Injury Observations 3.5 Foliage Chemical Analysis	6 8 9 9
4	Results 4.1 Foliage Chemistry 4.2 Statistical Analysis 4.3 Foliage Injury	11 18
5	Discussion 5.1 Calcium 5.2 Sodium 5.3 Chlorine 5.4 Fluorine 5.5 Inter-Element Relationships 5.6 Foliage Injury	27 28 31 32 35
6	Private Property Alleged Injury Investigations	40
7	7.2 Sodium Trends In Unwashed Silver Maple	49 49
8	Conclusions	52
9	Recommendations	54
1	0 References	55
	Appendix A	
	Appendix B	

List of Figures

1	Survey Stations - ACCL/GCCL Survey, 1987	7
2	Prevailing Wind Direction - Windsor	8
	Calcium in Silver Maple Foliage	13
4	Sodium in Silver Maple Foliage	14
5	Chlorine in Silver Maple Foliage	15
6	Fluorine in Silver Maple Foliage (uw)	16
7	Fluorine in Silver Maple Foliage (w)	
8	Calcium vs Chlorine in Silver Maple	
9	Sodium vs Chlorine in Silver Maple	21
10	Sodium vs Fluorine (uw) in Silver Maple	22
11	Sodium vs Fluorine(w) in Silver Maple	
12	Fluorine (uw) vs Fluorine (w) in Silver Maple	24
13	Seasonal Calcium in Silver Maple (uw)	
14	Seasonal Sodium in Silver Maple (uw)	
15	Seasonal Chlorine in Silver Maple (uw)	
	Seasonal Fluorine in Silver Maple (uw)	
	Seasonal Fluorine in Silver Maple (w)	

List of Tables

1	Survey Stations - ACCL/GCCL Survey, 1987	6
2	Silver Maple Foliage Chemistry-ACCL/GCCL Survey, 1987	12
3	Inter-Element Concentration Correlation Coefficients	18
4	Rank Values of Element Concentrations	25
5	Injury Rating of Silver Maple Foliage	26

1 Executive Summary

In 1987, the Phytotoxicology Section conducted a vegetation survey in the vicinity of the industrial complex occupied by Allied Chemical Canada Limited (ACCL) and General Chemical Canada Limited (GCCL) in Amherstburg, Ontario. This survey consisted of multiple samplings of silver maple foliage for chemical analysis and visual ratings of the severity of foliar injury attributable to atmospheric emissions from the industries. These activities were conducted at nine permanent stations at the end of the months of May through September.

The results of chemical analysis indicated highly elevated concentrations of fluorine, sodium and chlorine; in excess of the Phytotoxicology Section Upper Limits of Normal guidelines for unwashed foliage. Washed foliage from one station contained fluorine concentrations in excess of former Control Order limits on each sampling date.

The sources of these contaminants could be traced to the industrial complex, although a second industrial source of chlorine in the geographic area precluded ascribing all of the chlorine contamination to the ACCL/GCCL complex.

Visual examination of silver maple foliage frequently revealed trace levels of injury characteristic of fluoride or sodium chloride exposure. However, due to the similarity of injury symptoms caused by these contaminants, it was not possible to attribute the injury to one or the other.

A review and analysis of foliage chemistry data derived from six of the nine stations which have been active since 1975 indicated continuous and environmentally unacceptable contamination of silver maple foliage by emissions ascribed to the two companies. The consistent and excessive degree of foliar contamination during the past 12 years indicates that emission control initiatives at this industrial complex have not provided adequate protection to the surrounding terrestrial environment.

2 Introduction

2.1 Industrial Sources

Allied Chemical Canada Ltd. (ACCL) began operating at its Amherstburg plant location in 1919 to produce sodium carbonate. By 1985 the plant was involved in the production of four principal chemical products:

- 1. Sodium carbonate (Na_2CO_3) is produced from salt (NaCl) and limestone $(CaCO_3)$ using an ammonia catalyst. Operation began in 1919.
- 2. Calcium chloride dihydrate (CaCl₂.2H₂0) is produced through the refining of the calcium chloride and salt solution by-products from the sodium carbonate production. Operation began in 1934.
- 3. Fluorocarbons are produced from a reaction of hydrofluoric acid (HF) and carbon tetrachloride (CCl $_4$), with hydrochloric acid (HCl) as a by-product. Operation began in 1965.
- 4. Hydrofluoric acid (HF) is produced from a reaction of sulphuric acid (H_2SO_4) and fluorspar (CaF_2), with gypsum ($CaSO_4$) as a by-product. Operation began in 1971.

In 1986, a corporate reorganization resulted in the retention of the hydrofluoric acid and fluorocarbon production facilities by ACCL and the acquisition of the sodium carbonate and calcium chloride production facilities by General Chemical Canada Ltd. (GCCL). Both companies maintain operations at the same physical location, with GCCL assuming control of those parts of the physical plant related to sodium carbonate and calcium chloride production.

At some point in time, presumably after the reorganization, ACCL acquired the corporate name Allied Chemicals Canada Incorporated. For the purpose of this report, all references to Allied Chemical Canada Limited or ACCL should be interpreted as referring to the company now known as Allied Chemicals Canada Incorporated.

In 1982, a new industrial operation was established at a site immediately east of the ACCL/GCCL complex. Canada Occidental Petroleum Ltd. (formerly BCM Technologies Ltd. and now known as CanadianOxy Industrial Chemicals Limited Partnership) produces sodium chlorate (NaClO $_3$) by electrolysis of salt (NaCl) in an aqueous solution and oxidation of intermediate products to produce the sodium chlorate with H $_2$ gas as a byproduct. Principal fugitive emissions consist of gaseous chlorine and particulate salt and sodium chlorate from the receiving and shipping operations (Luyt, 1986).

The proximity of this new industry to the ACCL/GCCL complex and the similarity of potential emissions, with respect to common chemical elements, must, therefore, be acknowledged in the interpretation of environmental contamination ascribed to the ACCL/GCCL complex.

2.2 Phytotoxicology Section Surveys

The Phytotoxicology Section initiated vegetation surveys in the vicinity of the ACCL/GCCL industrial complex in 1970. The initial survey was a pre-operational background survey prior to the operation of the hydrofluoric acid production facilities. Vegetation monitoring surveys have since been conducted annually, during the summer growing periods. These surveys were designed to detect excessive concentrations of chemical elements in vegetation as a result of emissions from the industrial complex, as well as to identify occurrences of injury to vegetation which could be attributed to aerial exposure to specific elements or compounds used or produced at the industrial complex.

Vegetation surveys conducted in 1971 through 1973 revealed fluorine concentrations in vegetation which were highly elevated when compared to the pre-operational survey of 1970. Fluoride induced injuries to native vegetation and to gladiolus indicator plants were also observed (Linzon et al., 1973).

2.3 Control Orders

In 1974, ACCL was served with a Control Order under the Environmental Protection Act which set limits on the concentrations of fluorine which could be encountered in forage (grass) in the vicinity of the hydrofluoric acid production facility. A new Control Order was served in 1975 setting limits for fluorine concentrations in forage and silver maple foliage. This Control Order was in effect until 1977. Finally, in 1978 the third Control Order was served on ACCL. This Control Order was identical to the one served in 1975, except for the period of coverage.

This latest order, served on July 13, 1978, addressed the operation of the hydrofluoric acid plant. The order directed that emissions from the plant were to stop by discontinuing the operation of the plant upon notice from the Ministry of the Environment that the following conditions occurred:

- 1. Concentration of fluorine in unwashed forage collected within 3000 metres of the source exceeded 80 ppm in any one month of May through October.
- 2. Concentration of fluorine in unwashed forage collected within 3000 metres of the source exceeded an average of 60 ppm in any two consecutive months of May through October.
- 3. Concentration of fluorine in washed silver maple foliage collected within 3000 metres of the source exceeded 100 ppm in any one month of May through October.

However, the Control Order also stated that plant operations could continue if the Director was satisfied that concentrations for the remaining months would not be exceeded.

This latest order expired on October 31, 1978 and no other has been served to this date. Although the limits to the fluorine concentrations in vegetation set forth in the various Control Orders were exceeded before and during the

tenure of the Control Orders, and have continued to be regularly exceeded subsequent to the expiration of the 1978 Control Order, ACCL has not been ordered to suspend operations of the HF plant or related processes. The foliar contamination was not considered a threat to human health and therefore could not legally serve as a basis for plant shutdown.

3 1987 Phytotoxicology Vegetation Survey

3.1 Sampling Stations and Dates

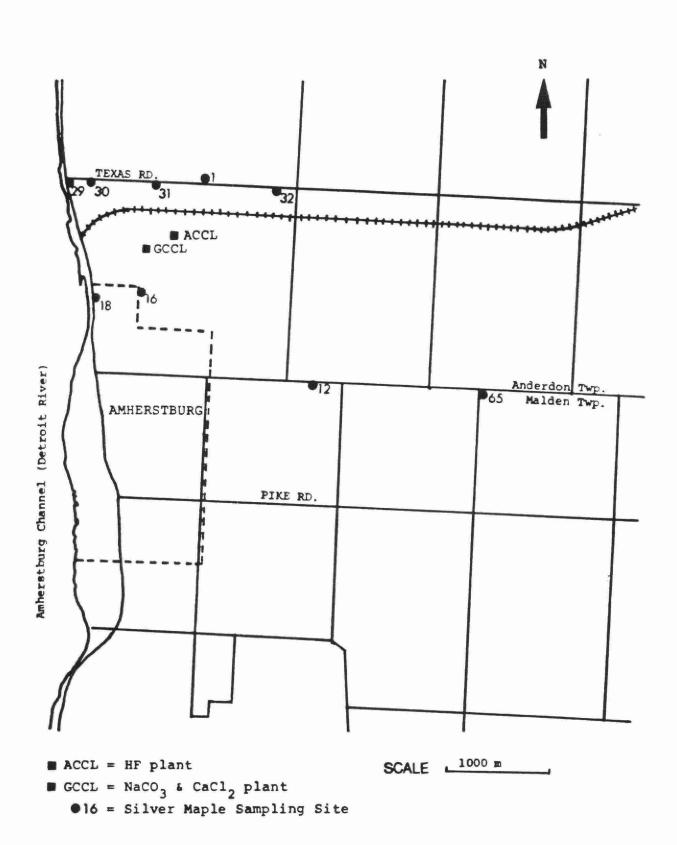
In 1987, the Phytotoxicology vegetation monitoring survey consisted of sampling silver maple (Acer saccharinum) foliage for chemical analysis and visually estimating the degree of foliage injury attributable to sodium chloride or fluoride exposure. There were nine stations in the survey, each consisting of a single sample tree which was sampled and visually assessed at the end of each month of May through September. Actual sampling and assessment dates were May 28, June 29, July 28, August 31 and September 30.

The locations of these stations are indicated in Figure 1 and the distances and compass bearings from the hydrofluoric acid plant are contained in Table 1. The HF plant was used as a reference point only and does not imply that it is the only source of atmospheric emissions within the industrial complex occupied by the two companies. The 1987 survey was unique since only silver maple foliage samples were collected at the end of each month. Previous surveys also involved collections of forage samples and included maple foliage collections from an expanded station network in August.

Table 1: Survey Stations - ACCL/GCCL Survey, 1987

Station Number	Distance (m)	Azimuth
1	590	30° NNE
12	1930	136° SE
16	640	212° SSW
18	980	231° SW
29	1160	295° WNW
30	970	302° WNW
31	500	336° NNW
32	1070	66° ENE
65	3300	114° ESE

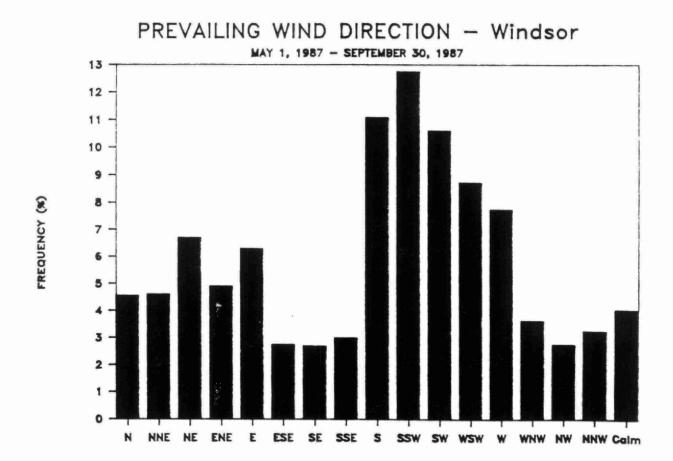
Figure 1: Survey Stations - ACCL/GCCL Survey, 1987



3.2 Prevailing Winds

Prevailing surface wind directions are critical to the distribution of emissions from the source industries. The nearest location, to the complex, where wind is recorded is at the Windsor airport. Figure 2 represents a frequency distribution of prevailing winds at Windsor and was compiled from hourly observations from May to September, 1987. These data were obtained from the Environment Canada, Atmospheric Environment Service, Monthly Meteorological Summary reports.

FIGURE 2



3.3 Foliage Sampling and Processing

Sampling consisted of cutting several foliated branches from the side of the tree facing the industrial complex using tree pruners on extension poles. The foliage from each branch was removed by latex-gloved hand and placed into polyethylene bags along with appropriate labels. Three replicate samples were obtained at each station.

The samples were transported to the Phytotoxicology Section sample processing laboratory where half of the foliage from each bag was subjected to a wash in a distilled water solution of 0.05% NaEDTA and 0.05% Alconox™ detergent followed by three separate rinses with distilled water. Both washed and unwashed subsamples were transferred to kraft paper bags and dried in a forced air oven at 80°C. Dry samples were ground in a stainless steel Wiley mill to pass through a 1 mm screen and collected in flint glass jars.

3.4 Injury Observations

At the time of sampling, the degree of injury to the foliage on the sampled branches was determined visually. Injury symptoms which consisted of a browning or blackening of the terminal margins were considered to be induced by fluoride or salt exposure. Injury ratings are, therefore, based on the foliage ultimately used for chemical analysis. Rating the injury to the collective foliage on the whole tree from ground level would not be reliable due to visibility constraints and was not attempted.

3.5 Foliage Chemical Analysis

Chemical analysis of the samples was performed by the MOE Laboratory Services Branch. Detailed analytical methods are contained in MOE (1983). In brief, the methods were as follows. Calcium and sodium were determined on strong acid digestions of the samples by Inductively Coupled Plasma

Emission and Atomic Emission Spectrop Temetry, respectively. Chlorine was determined by X-Ray Fluorescence Spectrophotometry. Fluorine was determined by Ion Selective Electrode on a 0.1 N perchloric acid sample extraction. Concentrations of the four elements were determined in the unwashed subsamples. Only fluorine was determined in the washed subsamples.

4 Results

4.1 Foliage Chemistry

The element concentration arithmetic means and standard deviations for each set of triplicate samples are tabulated for each sampling date and station in Table 2. All concentration data in this report are on a dry sample weight basis. It should be noted that, in a few cases, the concentrations of fluorine in washed and unwashed subsamples collected at the most distant station, Station 65, were reported as below the detection limits of 4 or 5 ug/g. For statistical analysis purposes, these data points were assigned values of one half of the reported detection limit. These estimated data points have been integrated into the Table 2 data summary and subsequent statistical analyses and graphic representations.

The element concentration means for each set of triplicate samples collected at each sampling station are graphically presented, by the month of sampling, in a series of five histograms, Figures 3 through 7. These represent the four elements in unwashed foliage and fluorine in washed foliage.

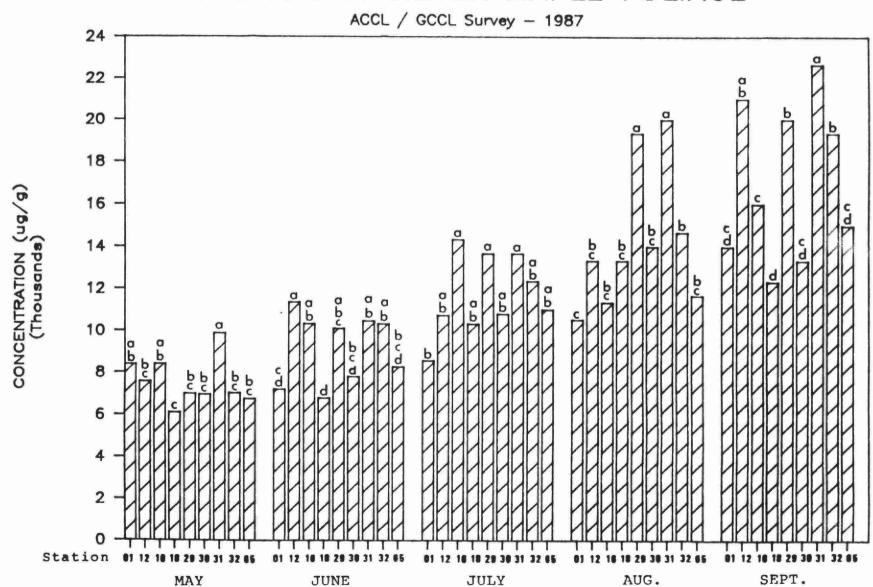
These histograms also contain indicators on the concentration axes which represent the Phytotoxicology Section Upper Limit of Normal Guidelines for urban (ULNu) and rural (ULNr) unwashed foliage samples, where such guidelines have been established. The washed fluorine histogram (Figure 7) contains an indicator (CO) at the 100 ppm mark of the concentration axis representing the maximum acceptable fluorine concentration in washed silver maple foliage as directed in the 1978 Control Order discussed previously.

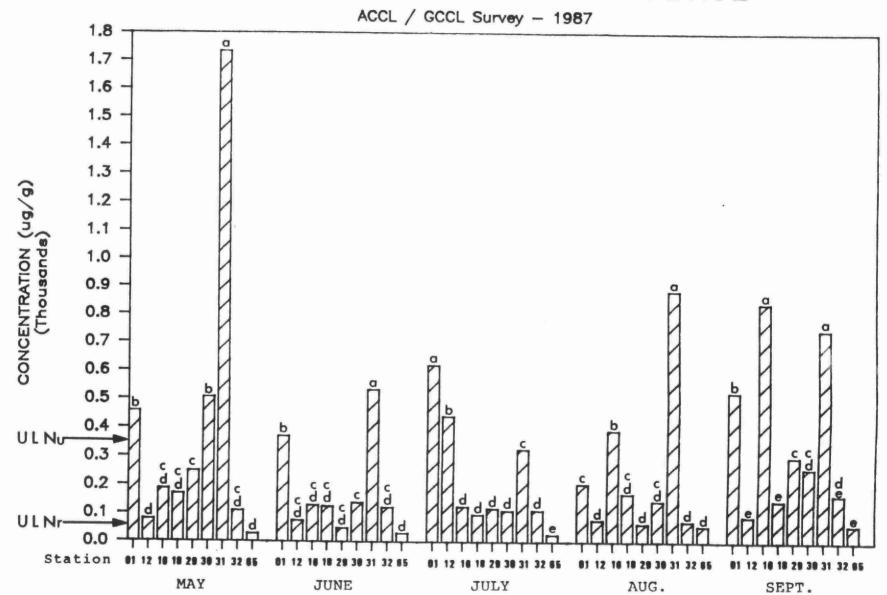
Table 2: Silver Maple Foliage Chemistry - ACCL: MICL Survey, 1987

	Ca (t Mean	1g/g) S.D.	Na (u Mean	1g/g) S.D.	Cl (%) Mean	F S.D.	uw (ug Mean S		F w (uc	
May 28										
Stn. 01 Stn. 12 Stn. 16 Stn. 18 Stn. 29 Stn. 30 Stn. 31 Stn. 32 Stn. 65	8400 7567 8400 6100 6967 6933 9867 7000 6733	927 998 698 510 858 499 189 1639 634	457 79 187 170 250 507 1733 110 27	94 9 17 22 37 78 170 8 3	0.20 0.07 0.38 0.17 0.24 0.17 0.34 0.08	0.01 0.00 0.03 0.02 0.00 0.02 0.03 0.01 0.01	346 15 69 59 29 44 156 44	49 2 8 6 2 2 25 1 2	194 8 38 29 17 18 61 32 3	38 1 2 6 4 2 3 2
June 29										
Stn. 01 Stn. 12 Stn. 16 Stn. 18 Stn. 29 Stn. 30 Stn. 31 Stn. 32 Stn. 65	7167 11333 10333 6767 10100 7800 10467 10333 8267	896 471 943 624 698 535 2317 2604 330	370 74 130 127 47 140 533 123 31	50 8 24 9 3 16 119 12	0.23 0.11 0.33 0.34 0.21 0.12 0.24 0.10 0.35	0.02 0.02 0.05 0.03 0.01 0.01 0.04 0.00 0.01	212 13 33 36 29 19 74 42 10	16 1 7 3 3 3 8 6 0	126 9 24 27 21 13 51 35	40 1 3 1 2 1 6 5 0
July 28										
Stn. 01 Stn. 12 Stn. 16 Stn. 18 Stn. 29 Stn. 30 Stn. 31 Stn. 32 Stn. 65	8567 10733 14333 10333 13667 10800 13667 12367 11000	2444 1969 471 1247 471 1883 2055 2310 816	620 440 127 98 120 112 327 113 26	29 54 19 26 0 14 39 12	0.35 0.13 0.40 0.25 0.28 0.08 0.26 0.11	0.05 0.01 0.05 0.02 0.04 0.02 0.05 0.00 0.05	311 11 34 29 95 43 86 42 8	67 1 2 9 15 7 11 4	161 9 18 18 42 14 29 28	25 0 2 2 6 2 9 1
August 31										
Stn. 01 Stn. 12 Stn. 16 Stn. 18 Stn. 29 Stn. 30 Stn. 31 Stn. 32 Stn. 65	10533 13333 11333 13333 19333 14000 20000 14667 11667	660 471 471 2055 2625 2828 1414 471 471	207 78 393 172 64 147 883 73 57	45 7 111 62 4 12 87 9	0.40 0.16 0.57 0.35 0.37 0.07 0.39 0.11	0.01 0.05 0.02 0.04 0.01 0.00 0.02 0.01	203 14 34 33 27 20 62 24	9 0 6 5 2 1 9 8 0	153 13 26 24 26 23 44 27	17 1 3 4 3 7 3 7 6
September 30										
Stn. 01 Stn. 12 Stn. 16 Stn. 18 Stn. 29 Stn. 30 Stn. 31 Stn. 32 Stn. 65	14000 21000 16000 12333 20000 13333 22667 19333 15000	1633 2160 816 943 816 1247 471 943 816	527 92 840 150 303 263 747 170 60	19 7 128 16 54 9 26 14	0.04 0.20 0.54 0.42 0.49 0.13 0.69 0.16	0.00 0.00 0.05 0.02 0.05 0.00 0.04 0.03 0.05	223 32 67 61 190 58 109 48 17	9 1 2 7 36 9 17 3	140 27 46 48 75 38 60 43 14	22 0 3 4 12 3 7 3

ULNr → (30,000 ug/g) FIGURE 3

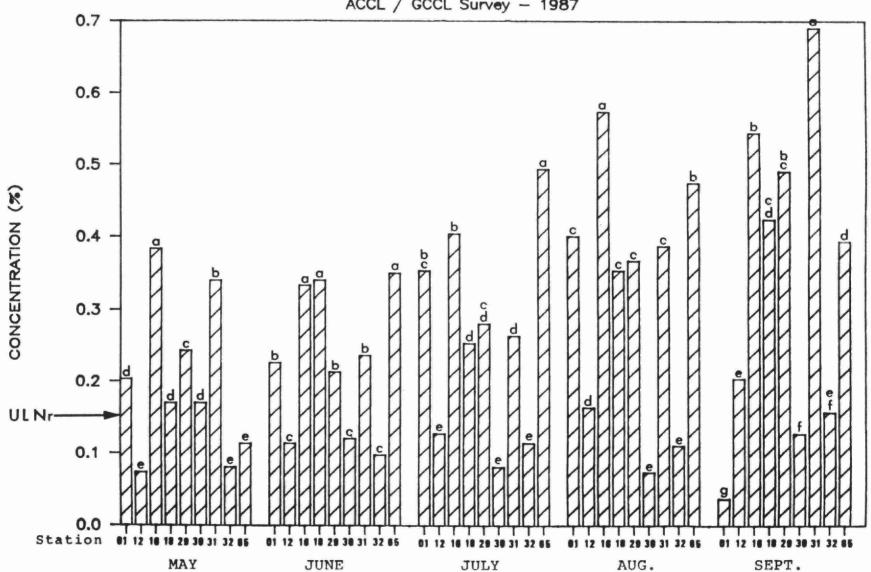
CALCIUM IN SILVER MAPLE FOLIAGE



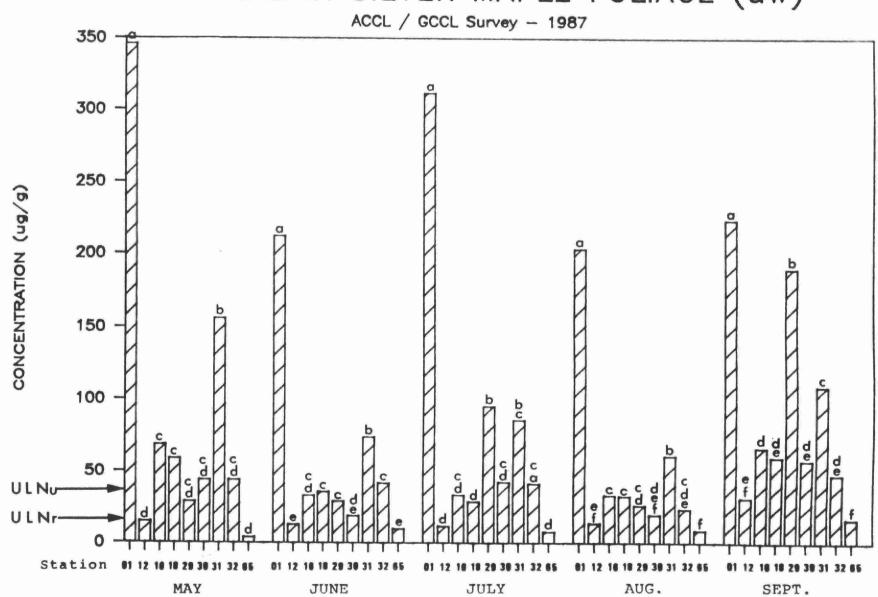


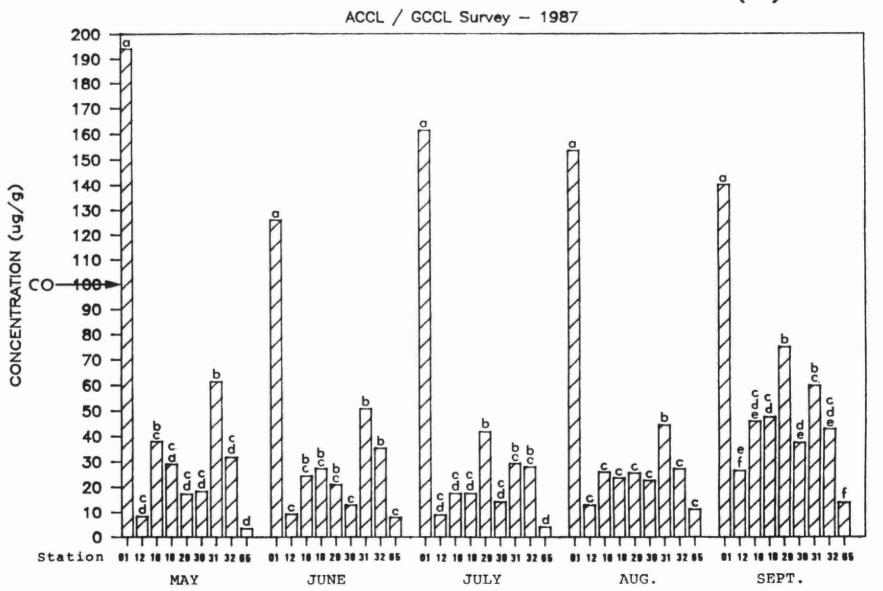
-14





FLUORINE IN SILVER MAPLE FOLIAGE (uw)





-17

4.2 Statistical Analysis

The Duncan's Multiple Range routine of SAS (1979) was used to determine if the concentrations of elements differed between the nine stations on each of the five sampling dates. Figures 3 through 7 contain alphabetic characters above each bar in the histogram distinguishing the Duncan groups. Bars with different characters indicate significantly different (p=0.05) concentration means for that sampling date.

To determine whether there were any relationships between the element concentrations in each sample, a series of linear regression analyses were performed using the regression analysis capabilities of Lotus 123 (Lotus 123, 1986). Table 3 is a matrix of correlation coefficients (r) for each pair (n = 135) of variables and indicators of the degree of significance.

Table 3: Inter-Element Concentration Correlation Coefficients (r)

	Sodium	Chlorine	Fluorine (uw)	Fluorine	(W)
Calcium	.126 ns	.351 **	.007 ns		.015 ns	
Sodium		.270 **	.450 **		.363 **	
Chlorine			.118 ns		.080 ns	
Fluorine	(uw)				.936 **	

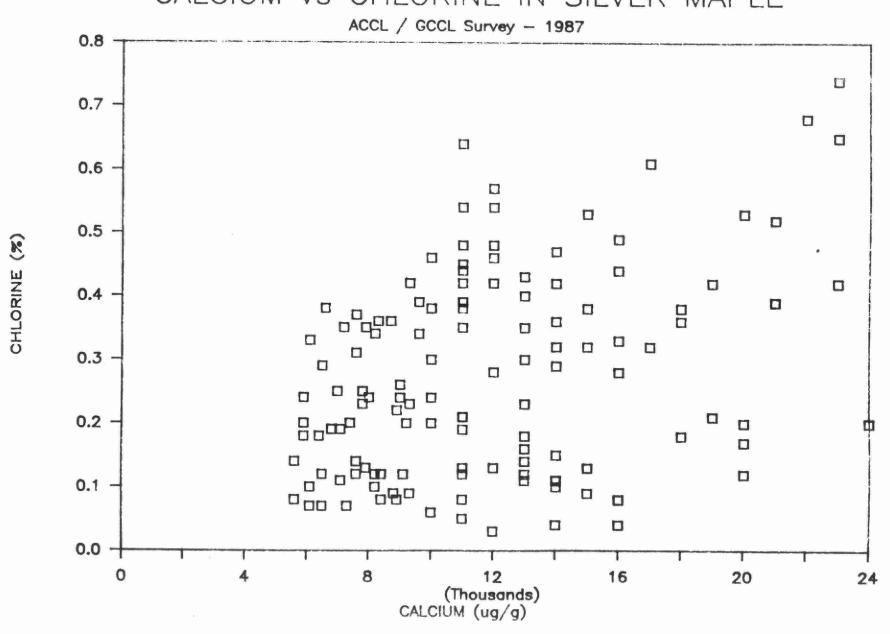
** = significant at p = .01 ns = not significant

Figures 8 through 12 are scatter plots of the individual sample analytical results for each pair of variables with a significant correlation. These plots are visual representations of the relationships between the different element concentrations in silver maple foliage samples.

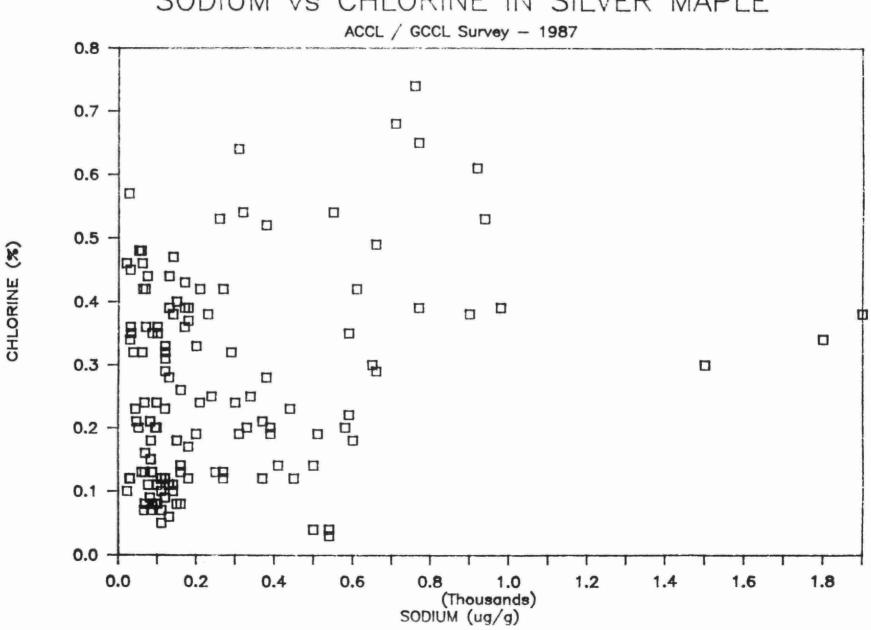
The concentration means for each of the nine stations were also ranked in order of magnitude for each sampling date. A Rank Value of "1" indicates that that station had the highest concentration of a particular element on that collection date. By ranking data for each of the five sampling dates and then summing the Rank Values for each station, it is possible to assess which station(s) had the most consistent high or low concentrations of the different elements. The relative differences between these Rank Totals indicate the consistency with which a station had high or low element concentrations. The Rank Totals can range from five, for a station that had the highest concentration of an element on each sampling date, to 45, for a station that had the lowest concentration on each sampling date. The monthly Rank Values as well as the seasonal Rank Totals for each station are presented in Table 4.

FIGURE 8

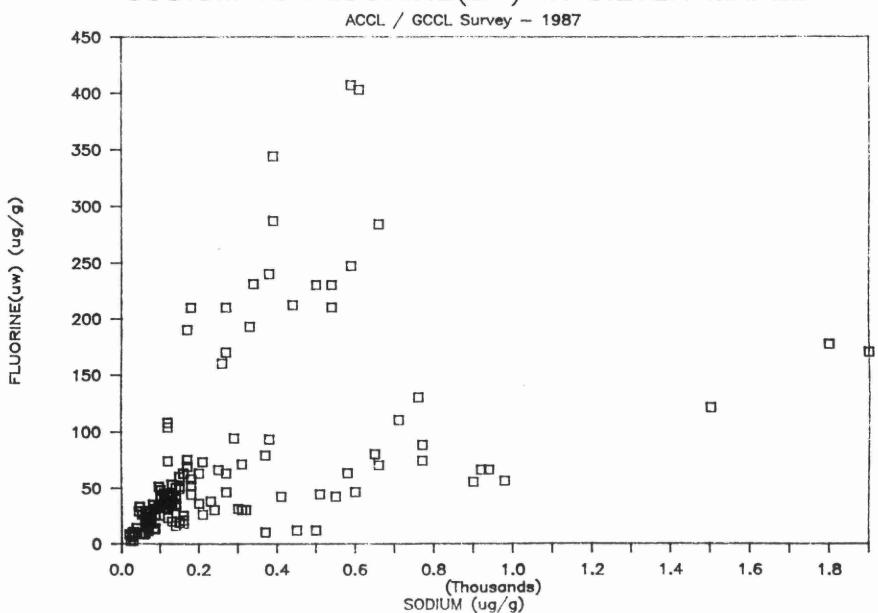
CALCIUM VS CHLORINE IN SILVER MAPLE



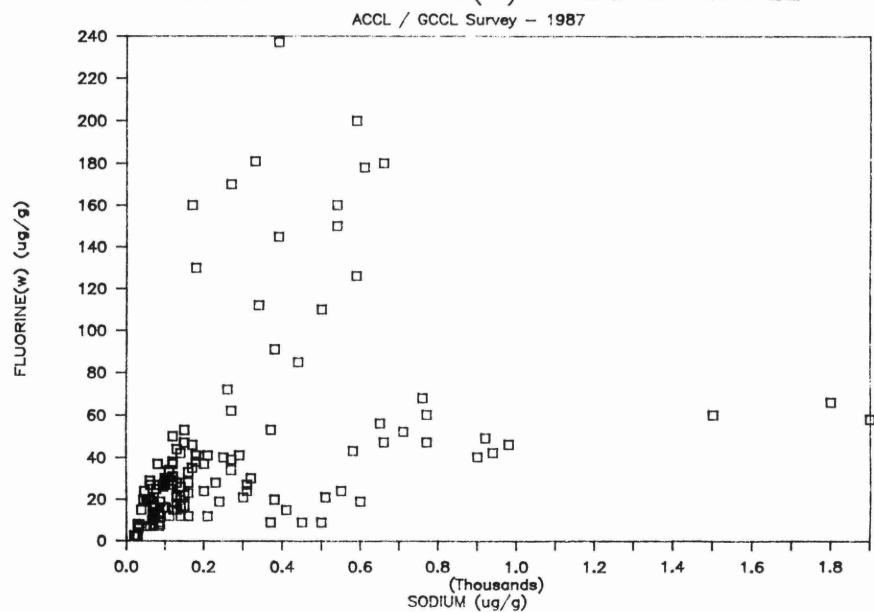
SODIUM VS CHLORINE IN SILVER MAPLE



SODIUM vs FLUORINE(uw) IN SILVER MAPLE



SODIUM vs FLUORINE(w) IN SILVER MAPLE



FLUORINE(uw) vs FLUORINE(w) IN SILVER MAPLE

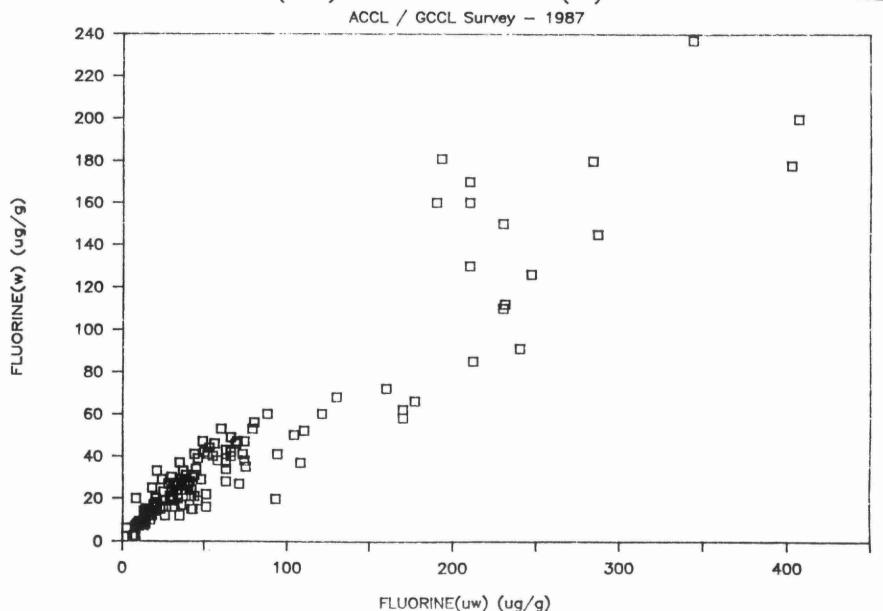


Table 4: Rank Values of Element Concentrations

		MAY	JUNE	JULY	AUG.	SEPT.	RANK DTALS
CALCIUM	Stn. 01 Stn. 12 Stn. 16 Stn. 18 Stn. 29 Stn. 30 Stn. 31 Stn. 32 Stn. 65	342967158	8 1 3 9 5 7 2 4 6	9 7 1 8 3 6 2 4 5	9 5 8 6 2 4 1 3 7	7 2 5 9 3 8 1 4 6	36 19 19 41 19 32 7 20 32
SODIUM	Stn. 01 Stn. 12 Stn. 16 Stn. 18 Stn. 29 Stn. 30 Stn. 31 Stn. 32 Stn. 65	3 8 5 6 4 2 1 7 9	27 4 5 8 3 1 6 9	1 2 4 8 5 7 3 6 9	3 6 2 4 8 5 1 7	3 8 1 7 4 5 2 6 9	12 31 16 30 29 22 8 32 45
CHLORINE	Stn. 01 Stn. 12 Stn. 16 Stn. 18 Stn. 29 Stn. 30 Stn. 31 Stn. 32 Stn. 65	4 9 1 6 3 5 2 8 7	5 8 3 2 6 7 4 9 1	372649581	3 7 1 6 5 9 4 8 2	9 6 2 4 3 8 1 7 5	24 37 9 24 21 38 16 40 16
fLUORINE (uw)	Stn. 01 Stn. 12 Stn. 16 Stn. 18 Stn. 29 Stn. 30 Stn. 31 Stn. 32 Stn. 65	1 8 3 4 7 6 2 5 9	1 8 5 4 6 7 2 3 9	1 8 6 7 2 4 3 5 9	1 8 3 4 5 7 2 6 9	1 8 4 5 2 6 3 7 9	5 40 21 24 22 30 12 26 45
FLUORINE (w)	Stn. 01 Stn. 12 Stn. 16 Stn. 18 Stn. 29 Stn. 30 Stn. 31 Stn. 32 Stn. 65	1 8 3 5 7 6 2 4 9	1 8 5 4 6 7 2 3 9	1 8 5 6 2 7 3 4 9	1 8 4 6 5 7 2 3 9	1 8 5 4 2 7 3 6 9	5 40 22 25 22 34 12 20 45

4.3 Foliage Injury

The foliage on sample branches which were used for chemical analysis was visually rated for symptoms of injury symptomatic of fluoride or salt exposure. The injury symptoms, which were considered to be due to the fluoride or salt, consisted of a blackening of the tips of the palmately lobed silver maple leaves. Injury which could be ascribed to physiological disorders, diseases or insects was not considered in the ratings. Table 5 summarizes the severity of observed fluoride or salt injury symptoms.

Table 5: Injury Rating of Silver Maple Foliage

	May	June	July	Aug.	Sept.
Stn. 01	-	TR	TR-LT	TR	-
Stn. 12	-	-	-	-	-
Stn. 16	-	-	TR	TR	TR
Stn. 18	-	TR	-	-	_
Stn. 29	TR	TR	TR	TR	TR
Stn. 30	-	TR	_	-	-
Stn. 31	-	TR	TR	TR	LT
Stn. 32	-	TR	_	-	-
Stn. 65	-	- ,	_	-	-

^{- =} not injured

TR = >0-1 % of foliage area injured LT = 2-10 % of foliage area injured

5 Discussion

5.1 Calcium

Figure 3, Calcium in Silver Maple Foliage, revealed a definite trend of increasing foliar concentrations from the May to the September samples. The highest concentration mean encountered was 23,000 ug/g. This was considerably lower than the Upper Limit of Normal guideline for rural samples of 30,000 ug/g.

The seasonal trend of increasing calcium concentration can be ascribed to physiological causes, synonymous with maturation of foliage. Unpublished data produced by the author indicate similar seasonal trends in calcium concentrations in maple foliage from sites remote from industry or urbanization.

However, this trend was not completely consistent. Several instances of lower calcium concentrations in a subsequent sampling were encountered. These apparent inconsistencies can be attributed to the habit of maples to continue production of new foliage throughout the growing season and the probability of sampling different proportions of old and new leaves during each station visit.

The Duncan Multiple Range test identified up to four different concentration groups for any given sampling date. No one station had consistently highest or lowest concentrations for all sampling dates. Station 31 did have a notably low Rank Total of seven, identifying it as the station with relatively high concentrations of calcium in the foliage. However, neighbouring Station 1 with a Rank Total of 36 had the second lowest concentrations. Both stations were downwind of the industrial complex.

Compounds containing calcium are used and produced at the industrial complex. Releases of these compounds, specifically calcium carbonate, do occur during the loading of the lime kilms operated by GCCL (Russell, 1988). These releases are not reported to the Ministry by the company, apparently because they occur with such regularity that they are considered part of the normal operating conditions at the plant.

These acknowledged releases did not manifest in identifiable foliar concentration elevations. This is probably a result of a combination of high background concentrations of calcium in foliage, limited foliar absorption and raininduced foliar washing of the calcium dusts.

It is unlikely that foliar injury by calcium will be induced due to its low toxicity. The use of silver maple foliage as a monitor of fugitive calcium dust exposure in the ACCL/GCCL survey area should be reconsidered.

The most probable long term environmental effect of these releases would be the increase of soil pH if the emissions are in the form of alkaline calcium compounds. The significance of this potential effect as well as the effects of chronic exposure of perennial vegetation by these alkaline dusts has not been determined.

5.2 Sodium

The most significant observations regarding the concentrations of sodium in silver maple foliage (Figure 4) were the extremely wide range in the concentrations encountered during this survey and the frequency and magnitude with which these concentrations exceeded the Upper Limit of Normal guidelines. Excluding the control Station 65 and the relatively remote Station 12, the concentration means ranged from 47 ug/g for Station 29 in June to 1733 ug/g for Station 31 in May. The rural ULN guideline of 50 ug/g was exceeded on 41 out of the possible 45 (5 sampling dates x 9 stations) occasions. Of the remaining four, three were for samples collected at the control Station 65. The urban ULN guideline of 350 ug/g was exceeded on 12 of the possible 45 occasions.

Residual salt in soil from road deicing operations can be a source of sodium in foliage; however, the pattern of sodium contamination of sampled trees in the ACCL/GCCL survey area does not implicate road salt as a major source of foliar contamination.

The Duncan Multiple Range test identified Station 31 as having concentrations in the highest group on four of the five sampling dates. The control Station 65 concentrations were assigned to the group with the lowest means on all sampling dates. The mean ranking procedure confirmed these trends, producing a Rank Total of eight for Station 31 and a Rank Total of 45 for Station 65. It also identified Stations 1 and 16, with Rank Totals of 12 and 16 respectively, as additional stations with consistently high concentrations of sodium in the foliage.

The wide variation along with notably higher sodium concentrations at selected stations suggest episodic releases of sodium compounds. The elevated concentrations at Stations 1 and 31 are consistent with the prevailing southwesterly winds (Figure 2) transporting sodium emitted from the industrial complex toward these stations. However, Station 16 is upwind of the prevailing direction, but relatively close to the sodium operations of GCCL (Figure 1). Closer examination of Figure 4 reveals that sodium at Station 16 was notably higher in August and especially in September than during the first three sampling dates. This supports the hypothesis that sodium releases are episodic, with these August and September increases probably due to releases during periods of northerly winds.

An additional suggestion of episodic and in this case significant releases of sodium is contained in the exceptionally elevated concentration of sodium encountered at Station 31 during the May sampling. The concentration mean encountered was 1733 ug/g, approximately twice as high as

any other such observation at this station, which had the most consistently high sodium concentrations. It should be noted that the analytical results for all three May/Station 31 replicate samples were consistent. Two adjacent stations, Station 1 to the east and Station 30 to the west, also had highly elevated sodium concentrations, 457 ug/g and 507 ug/g, respectively, on this sampling date. These observations suggests a major release of sodium prior to the May 28 sampling date which primarily impacted Station 31, and to a lesser extent, the adjacent stations. Subsequent samples from Station 31 had much lower concentrations, indicating washing of foliar surface deposits, leaching of foliar absorbed sodium by rain, or a combination of the two processes. Another possibility for the subsequent reduction in sodium concentrations at this station is the growth of new unexposed foliage and the concomitant dilution effect.

Whether such a release did occur is not known since no notice of such an occurrence was received by the Phytotoxicology Section or by the Windsor District Office (Gibson, 1988).

The evidence for episodic emissions of sodium compounds does not preclude the probability of chronic lower level emissions of sodium. It should be recalled that the concentrations encountered frequently exceeded the ULN guidelines. The sodium release episodes, however, are the dominant factor in the excessive contamination of silver maple, and in all probability, other foliage.

Possible contributions of sodium from the operations of Canada Occidental Petroleum are indicated as elevated foliar sodium concentrations at Stations 12 and 65. The later is considered a control station for the ACCL/GCCL survey. Concentrations at these stations commonly approached or exceeded the rural ULN guideline of 50 ug/g. On one occasion, Station 12 in July, the concentration exceeded the urban ULN

guideline of 350 ug/g. Station 12 is the closest station to this company and sodium releases from the shipping and receiving operations could impact on this station during periods of northwesterly winds.

5.3 Chlorine

Concentrations of chlorine in silver maple (Figure 5) are also characterized by an extremely wide range and a large number of occurrences, 32 of a possible 45, where the concentration exceeded the rural Upper Limit of Normal guideline of 0.15%. There is no urban ULN guideline.

Chlorine contamination can occur as a result of road deicing operations. However, as was the case for sodium, the pattern of chlorine contamination of the sampled trees does not implicate road salt as a major source of foliar chlorine.

The Duncan Multiple Range test failed to identify any one station with chlorine concentrations falling consistently into either the highest or lowest concentration group. Station 16 concentrations were in the high group on three occasions. Station 32 concentrations were in the low group on four occasions and Stations 12 and 30 concentrations were in the low group on three occasions each. Meanwhile, the control Station 65 concentrations were in the high group twice and the low group once. The mean concentration ranking procedure identified Station 16 as having the most consistently high chlorine concentrations with a Rank Total of nine; followed by Stations 31 and 65, both with a Rank Total of 16. Stations 32, 30 and 12 had the lowest Rank Totals, 40, 38 and 37 respectively.

The results of these analyses indicate that no clear pattern of chlorine contamination of silver maple foliage exists. Downwind stations frequently had the lowest chlorine concentrations. Meanwhile, the control Station 65 had the highest chlorine concentrations on two of the five sampling

dates. Since the ULN guideline was exceeded so frequently, a source of chlorine is indicated. The pattern of foliar chlorine concentrations, or lack thereof, fails to suggest where this source is located. Any attempt to explain this complex pattern would be speculative.

It should be recalled that both ACCL and GCCL use and manufacture compounds containing chlorine. In addition, a separate and probably significant source of chlorine exists in Amherstburg, namely Canada Occidental Petroleum Ltd.

Emissions from this source consist of sodium chloride and sodium chlorate particulates and chlorine gas (Luyt, 1986). Since the sodium compounds are in particulate form and are released at ground level, their zone of influence would be restricted to the source area. The chlorine gas, however, would have a much wider zone of influence. This chlorine may very well be a significant contaminant of vegetation in the general Amherstburg area. It is not possible to assign relative contributions of chlorine to the environment to the three potential sources with the current survey design.

A relatively weak but still noticeable trend does exist in foliar chlorine concentrations. This trend is visible in Figure 5 as a tendency towards higher chlorine concentrations with later sampling dates. A similar trend was seen in the calcium data which was ascribed to physiological causes. In the case of chlorine, physiological causes, if any, are likely secondary due to the exceptionally high concentrations, exceeding the ULN guideline, and the wide range of concentrations during any sampling date. The trend suggests accumulation of atmospheric chlorine by the foliage with the variation due to inconsistent age of the sampled foliage and imbalances in rates of accumulation or loses by the foliage.

5.4 Fluorine

The concentrations of fluorine in unwashed and washed silver maple foliage are represented in Figures 6 and 7,

respectively. The rural ULN guideline of 15 ug/g for unwashed foliage was met or exceeded on every occasion except on four of the five sample collections at control Station 65 and three of the five sample collections at Station 12. Station 12 is upwind of the ACCL HF plant and is the most remote (excluding the control) station from the HF plant. The urban ULN guideline of 35 ug/g was exceeded on 24 of the possible 45 occasions. Exceedences occurred at all stations except Stations 65 and 12.

Fluorine concentration in washed silver maple foliage was one of the limits set forth in the 1978 Control Order. The limit of 100 ug/g was exceeded at Station 1 on each sampling date. The highest concentration (194 ug/g in May) was almost twice the former Control Order limit. All remaining stations fell below this limit. To confirm the validity of these exceptionally high concentrations, a silver maple tree approximately 30 metres from Station 1 was sampled in September. This single sample was determined to contain 240 and 170 ug/g fluorine based on unwashed and washed subsamples respectively. These values are consistent with the triplicate means of 223 and 140 ug/g, unwashed and washed respectively, determined for Station 1 in September.

The Duncan Multiple Range test on unwashed foliage fluorine data placed all samples from Station 1 into the highest concentration group on each sampling date. This group contained only Station 1 samples. This test further identified Station 31 as the station with concentrations in the second highest group on four of the five sampling dates. Stations 12 and 65 were consistently placed into the lowest concentration group. This test produced very similar groupings for the washed foliage fluorine data. The only difference was the placement of Station 31 in the second highest group on all occasions. The ranking procedures simply

confirmed Stations 1 and 31 with the highest and Stations 65 and 12 with the lowest concentrations of fluorine in both washed and unwashed foliage.

This analysis clearly identifies the ACCL/GCCL complex as a source of significant contamination of silver maple by fluorine. The most proximal and downwind stations have the highest concentrations of fluorine, while the most remote and upwind stations have the lowest concentrations. The only industrial sources of fluorine in the Amherstburg area are associated with the operations of ACCL. However, the Phytotoxicology Section did not receive reports of unusual releases of this contaminant.

Upon excluding the high (1 and 31) and low (12 and 65) stations, fluorine concentrations in unwashed foliage at the remaining stations were in a relatively narrow range of from 19 to 95 ug/g with the exception of Station 29 in September. Chronic emissions of fluorine together with acute episodes which induce increases in foliar fluorine concentrations at specific stations over the course of the sampling period are indicated.

5.5 Inter-Element Relationships

Table 3, a correlation matrix between the foliar elements, reveals five pairs of elements with significant correlations. Ranked in order of the correlation coefficient (r), these pairs include:

- 1. Fluorine (uw) vs. Fluorine (w)
- 2. Sodium vs. Fluorine (uw)
- 3. Sodium vs. Fluorine (w)
- 4. Calcium vs. Chlorine
- 5. Sodium vs. Chlorine

Figures 8 through 12 are scatter plots of the individual sample concentrations for each of the significantly correlated pairs of elements. With the exception of the relationship depicted in Figure 8, a plot of the unwashed versus washed foliage fluorine concentrations, the correlation coefficients between the elements are not high (r<0.5), nor do the plots indicate strong relationships. However, due to the large number of samples (n = 135), these correlations are statistically significant.

When the samples containing the unusually high sodium concentrations are removed (Station 31 in May), the correlation coefficients between sodium and both forms of fluorine improve. However, the correlation coefficient between sodium and chlorine does not. This later observation is indicative of the independence of sodium and chlorine emissions. These emissions are either not exclusively sodium chloride or there is an independent source of one of the elements, such as chlorine from Canada Occidental Petroleum, or a combination of these conditions.

The strong correlation between the fluorine concentrations in unwashed and washed foliage is not in itself a significant observation. If the source of fluorine was the soil, laboratory washing would leach a proportion of the fluorine and the correlation would remain strong. What is significant in this analysis are the large differences in concentrations between the two sample types. Laboratory washing removed an average (all stations and dates) of 40 percent of the fluorine. This suggests atmospheric sources of fluorine deposited to the foliage, with a substantial portion of the fluorine removable by washing.

The significant correlation of sodium with both forms of fluorine are indicative of common sources for these contaminants. However, since these elements are not involved in any common industrial processes, their emissions must be independent. Since the correlations are relatively poor, it is probable that emissions are not continuous, but consist of intermittent, acute releases. The points of impingement are dependent on the prevailing winds during these emission episodes. Such releases of sodium were hypothesized in the discussion of the exceptionally high sodium concentrations encountered at Station 31 in May.

Releases of fluorine may also consist of acute episodes as may occur during production upsets. However, since fluorine concentrations at any given station had a tendency to maintain their high, intermediate or low rank characteristics throughout the sampling period, chronic emissions are indicated as a significant cause of the elevated levels.

The significance of the calcium versus chlorine correlation might also suggest common sources. However, calcium concentration patterns were ascribed mainly to physiological causes. Furthermore, the independent source of chlorine in the area precludes ascribing all chlorine contamination to the ACCL/GCCL complex. The reason for the significance of the correlation is probably due to common trends of increasing concentrations of both elements with progressively later sampling dates. In the case of chlorine, bioaccumulation in the foliage is indicated.

The weakest of the statistically significant correlations is between sodium and chlorine. However, the second source of chlorine together with increasing and decreasing chlorine concentrations at a given station between sampling dates makes it difficult to implicate salt (NaCl) as the sole form of either sodium or chlorine emissions. Some of the industrial processes, discussed in the Introduction, use salt as a raw material. In addition, various sodium and chlorine compounds are used or produced. Consequently, sodium and chlorine could be emitted in a variety of compounds, including NaCl.

5.6 Foliage Injury

Rating foliar injury is a subjective procedure and the results of such ratings must be interpreted with caution. In this survey the sample branches were the basis of the ratings and therefore the ratings do not apply to the whole of the tree constituting the sample station. There is a possibility that due to chance, a set of sample branches may have contained injury symptoms on one sampling date but a set of branches from the same station taken on a subsequent date did not have the symptoms. Consequently, the analysis of injury ratings, as contained in Table 5, must be restricted to an analysis of trends which could identify stations which were recorded as containing foliar injury most consistently.

It must also be noted that since the sample trees are of variable age, occur in different habitats and are genetically different, their susceptibility to injury due to fluorides and salt would not be identical. Furthermore, injury symptomatology caused by exposure to these two types of contaminants is very similar, consisting of marginal necrosis.

The injury ratings as recorded in Table 5 are generally in the 'trace' category. This indicates that the extent of injury was less than two per cent of the foliage area. On two occasions the degree of injury was slightly greater. Stations 12 and 65 were recorded to be free of injury due to airborne contaminants at all observation times. Station 29 exhibited injury on all five occasions. Stations 1, 16 and 31 exhibited injury on either three or four occasions. The remaining stations were recorded as injured on one occasion each.

Bernstein (1980) notes that if sodium or chlorine foliar concentrations exceed 0.2 or 0.5 percent, respectively, in fruit trees, then injury can usually be attributed to these contaminants. Assuming that silver maple has similar tolerances, it should be noted that sodium concentrations encountered during this survey were, with one exception, less than 1000 ug/g (0.1%). Chlorine concentrations did approach or exceed the 0.5% level on several occasions, but it should be noted that one sampling station that had typically high chlorine concentrations was the control station and no injury was reported.

NAS (1971) suggests that susceptible plants exhibit injury symptoms when foliar fluorine concentrations are in the range of 20 to 150 ug/g. Resistant plants can tolerate fluorine concentrations of 4000 ug/g without visible injury. Silver maple is considered to have intermediate sensitivity to fluorides.

In this survey the highest fluorine concentrations were reported at Station 1 in May, yet the foliage was injury free. Station 29 was reported to contain injured foliage on each sampling date while fluorine concentrations in unwashed foliage ranged from 27 to 190 ug/g. There is a lack of a clear relationship between injury and fluorine concentrations.

Consequently, it is not possible to definitively ascribe the marginal necrosis injuries observed to either fluorides or the sodium or chloride components of salt. Differences in susceptibility between individual trees as well as the possibility of synergistic interaction effects of the contaminants may, in part, account for this.

6 Private Property Alleged Injury Investigations

In 1987, the Phytotoxicology Section received requests for investigations of vegetation injury from eleven property owners in the vicinity of the ACCL/GCCL complex. All of these requests concerned properties on Texas Road which is an east-west road immediately adjacent to and north of the industrial complex. The investigations on six of the properties revealed a variety of insect, disease and physiological causes for the injuries. Injury due to air pollutants could not be identified on these six properties.

The remaining five properties were all adjacent to each other and backed onto the ACCL/GCCL complex boundary in the immediate vicinity of the hydrofluoric acid and sodium carbonate and calcium chloride plants. The vegetation on these properties consisted of a large number and variety of fruit and ornamental trees. Foliar injury on these plants consisted of varying degrees of marginal necrosis.

Four of these investigation requests were forwarded to the Phytotoxicology Section by GCCL personnel on June 29, 1987. GCCL had received complaints of vegetation injury from these property owners on June 1, 1987. The complaints were precipitated by an accidental release of ammonia by GCCL on May 29, 1987, the odour of which could be detected by the property owners. This release was confirmed verbally by GCCL personnel. The fifth investigation request was received by Phytotoxicology investigators on June 29, 1987, during investigations of the four original requests.

These investigations concluded that the foliar injury to fruit and ornamental trees was due to fluoride or salt exposure. There was no evidence of injury caused by ammonia vapour.

A second ammonia release by GCCL occurred on July 31, 1987. No allegations of vegetation injury on private property were received by the Phytotoxicology Section as a consequence of this release. According to the GCCL letter to the Ministry acknowledging this release, the wind at the time was easterly and therefore the released ammonia would not impact on private properties.

Since no other abnormal releases of other materials by either ACCL or GCCL were reported to the Phytotoxicology Section, it must be concluded that the injuries on the five properties were the result of previous acute or chronic emissions of fluorides and salt. The first ammonia release and associated odour may have been a catalyst for the property owners to examine their trees and request the investigations.

7 Review of Historic Silver Maple Foliage Chemistry Data

As discussed in the Introduction, the Phytotoxicology Section has been conducting vegetation surveys in the vicinity of the ACCL/GCCL complex since 1970. These surveys have traditionally included silver maple foliage injury rating and sampling for chemical analysis. The current configuration of sampling stations was established in 1975. Prior to 1975, the survey consisted of stations along three radii extending from the industrial complex. Six of the nine 1987 stations have been sampled consistently since 1975 at the end of each month during the growing season. These stations (numbers 1, 16, 18, 29, 30, and 31) are the most proximal to the complex and are located along Texas Road to the north and in a residential area to the south of the complex (Figure 1). A list of Phytotoxicology Section reports on these annual surveys is given in Appendix A.

The chemical analysis of these historic samples have usually included the same elements as determined in the 1987 survey. In some years, however, a particular element either was not analyzed (eg. calcium in 1975), was not reported in that year's report or subsequent reports (eg. sodium in 1978), or the element was determined on samples which were washed when more recent surveys did not include washing (eg. chlorine in 1975). These historic data as well as the 1987 data have been compiled in Appendix B. Also included are available historic data for other stations active in 1987 (Stations 12, 32 and 65), to serve as an up to date data base for time trend analyses should this survey be continued and include these stations.

Of the sample analyses performed at the six long term stations, only fluorine in washed foliage has a complete record. This is due to the primary concern with fluoride emissions

during the early years of this survey and subsequent monitoring for compliance with the Control Orders which cited limits of fluorine in washed silver maple foliage.

Figures 13 through 17 are histograms of the seasonal average foliar concentrations of the four elements in unwashed silver maple foliage and fluorine in washed silver maple foliage. These averages are based on all samples collected at each of the six stations during the respective annual survey period, ie. six stations over five months. There are exceptions in 1977 and 1978 when all analyses were not performed on the May samples. The averages are for the available data from those years.

Reviewing the mean seasonal foliar concentrations from these six stations will provide a mechanism for assessing the effectiveness of control measures initiated by the company or companies as measured by contamination of silver maple foliage. Short term variables such as wind directions, timing of accidental releases, rainfall washing of foliage etc. are minimized.

SEASONAL CALCIUM IN SILVER MAPLE (uw)

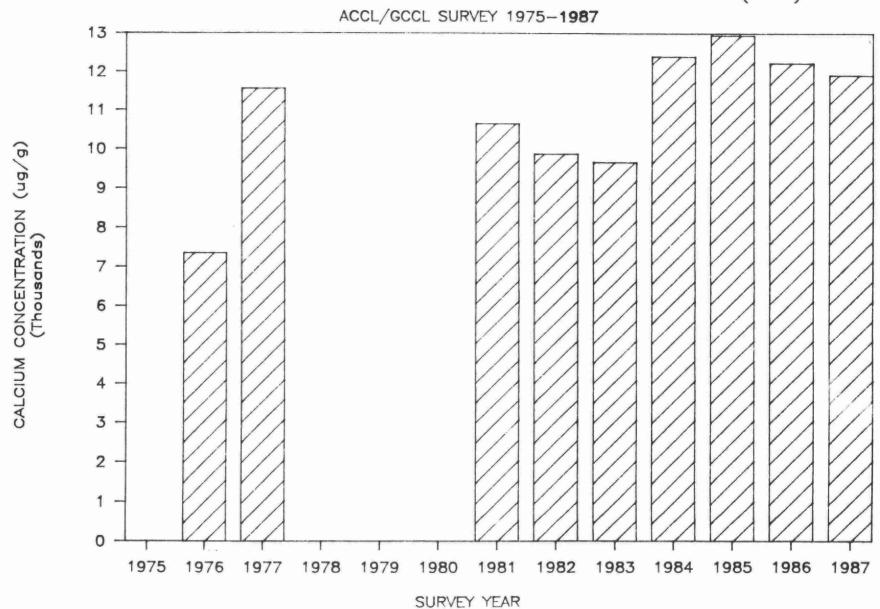
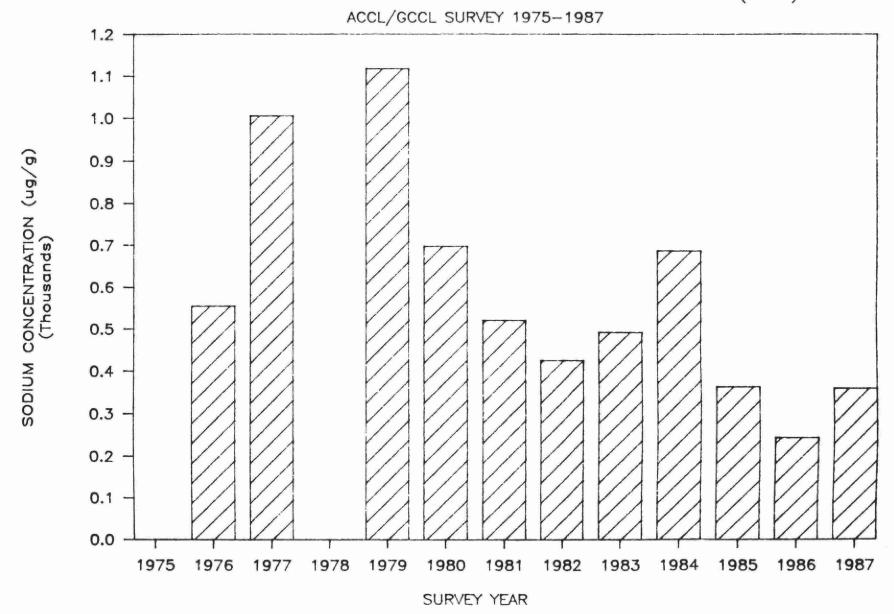


FIGURE 14

SEASONAL SODIUM IN SILVER MAPLE (uw)



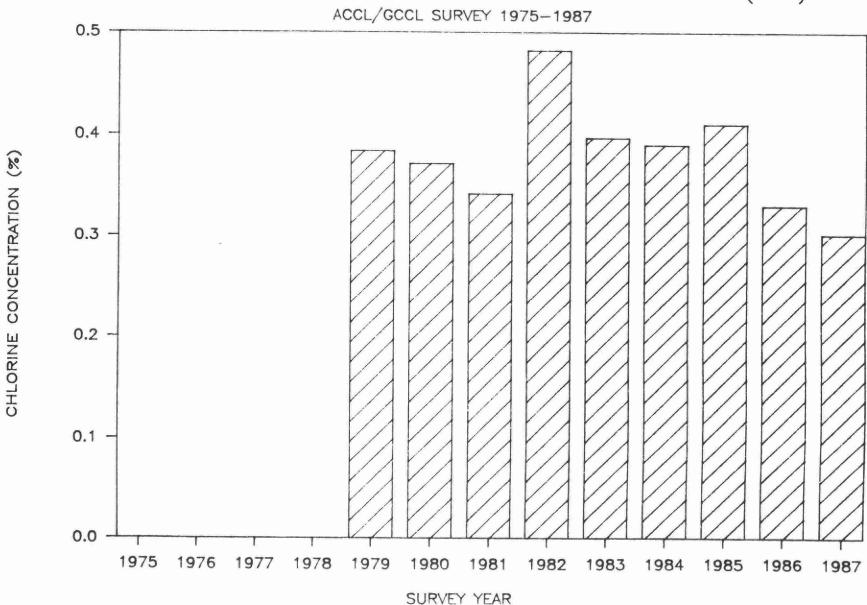
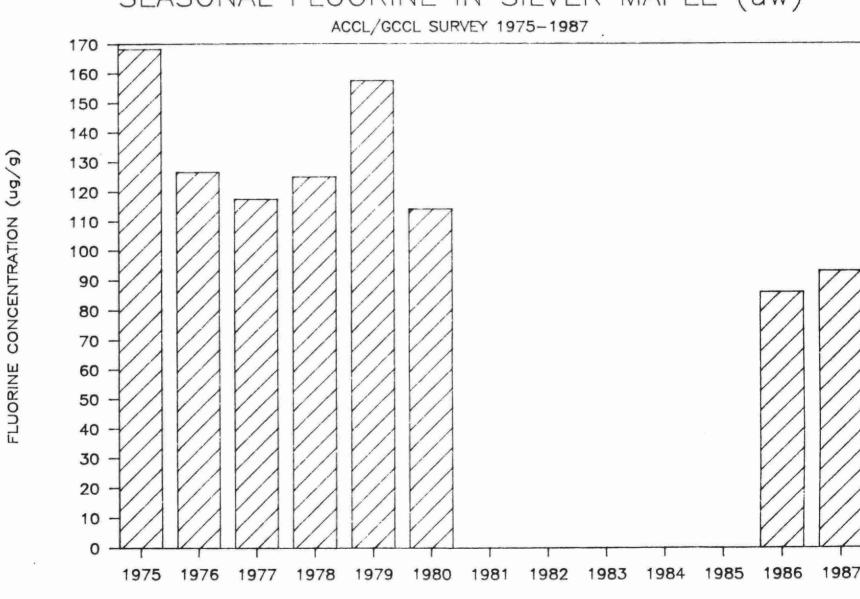
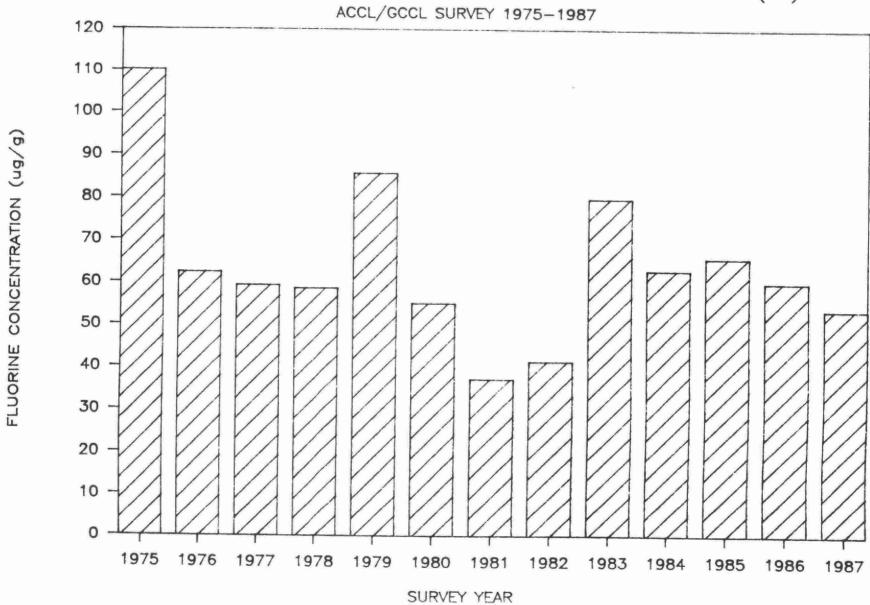


FIGURE 16

SEASONAL FLUORINE IN SILVER MAPLE (uw)



SURVEY YEAR



-48

7.1 Calcium Trends in Unwashed Silver Maple

Figure 13 indicates, with the exception of 1976, relatively constant concentrations of calcium over the years. Seasonal mean concentrations range from 10,000 to 13,000 ug/g. The seasonal trend of increasing concentrations through the growing season have been maintained, again with the exception in 1976 (see Appendix B). This strengthens the argument for physiological control of calcium concentrations overriding contributions from aerial contamination. While contamination by calcium emitted by the industry may be occurring, the high background concentrations, 1.0 to 1.3 % as dry weight, causes this potential contamination to be indiscernible by total foliage analysis.

The 1976 exceptions were due to very low September calcium concentrations at all six stations. This has reduced the seasonal average and negated the within-season trend. The original laboratory results report for the September 1976 sampling gives these low values. In the absence of another explanation for this discrepancy, it is probably due to an error in the analytical laboratory, either human or instrumental.

7.2 Sodium Trends In Unwashed Silver Maple

Sodium concentrations, Figure 14, have had considerable variation from year to year. Seasonal means exceeded the 350 ug/g urban ULN guideline in every year except 1986 and the rural ULN guideline of 50 ug/g in every year, frequently by an order of magnitude or more. These exceedences, along with the year to year variation, demonstrate that emissions of sodium compounds are a continuing source of contamination of silver maple foliage. This problem was especially severe in 1977 and 1979. The seasonal mean of 1987 is the second lowest since 1975 but even this mean still exceeds the urban ULN guideline. While notable reductions followed the peak in 1979, these were then followed by increases in 1983 and

1984. The contributions of sodium released by Canada Occidental Petroleum are inconsequential in this time trend analysis since the stations under consideration are well removed from this ground level, particulate source of sodium.

The cause of these cyclical variations is not known. Variations in industrial production rates together with ongoing chronic emissions may be one cause. Frequencies of uncontrolled releases in different years may be another.

7.3 Chlorine Trends in Unwashed Silver Maple

Seasonal mean chlorine concentrations, Figure 15, have remained relatively constant over the years with the exception of a moderately high peak in 1982 and moderate reductions in 1986 and 1987. The 1982 peak may be indicative of the start-up of the Canada Occidental Petroleum plant, although the Certificate of Approval was issued in October, 1982 and therefore after the sampling period. The actual date of start-up has not been confirmed by the author of this report.

The arrival of this new source of chlorine in the area makes it impossible to analyze the trend for chlorine emissions from the ACCL/GCCL complex. A moderate decline appeared to be developing between 1979 and 1981 but was interrupted by a notable increase in 1982. The 1987 concentrations are the lowest to date and suggest improved emission controls are having the desired effect.

However, the rural ULN guideline for chlorine of 0.15 % is regularly exceeded, even by seasonal means, by factors of two or three. Considerable reductions are still required before the ULN guideline is reached.

7.4 Fluorine Trends in Unwashed and Washed Silver Maple

When Figures 16 and 17, depicting fluorine concentrations in unwashed and washed foliage, are compared, it.

becomes apparent that variations in the seasonal foliar concentrations of fluorine in both sample types coincide. This is indicative of an airborne source of fluorine with foliar absorption of a portion of the contaminant. There is, however, no indication of a trend toward reduced concentrations since 1976.

The 1987 seasonal mean of fluorine in washed foliage is very similar to the mean encountered as early as 1976. If foliar concentrations are used as a measure of the effectiveness of emission control strategies implemented by the industry, then it would appear that significant emission reductions have not occurred for 11 years. In the interim, washed foliage fluorine concentrations have been higher or lower than those encountered in 1976 and 1987. Reasons for these variations could be similar to those for the sodium variations which are believed to relate to the frequency, timing and magnitude of emissions.

While there are no ULN guidelines for washed foliage, the former Control Order limit of 100 ug/g fluorine in washed silver maple foliage can be used as a measure of significant foliar contamination. In 1975, even the seasonal mean exceeded this limit. Since then, only in 1981 and 1982 were there no individual exceedences of this limit. These years also had the lowest seasonal means.

The Phytotoxicology Section ULN guidelines for fluorine in unwashed foliage are 35 ug/g for urban samples and 15 ug/g for rural samples. Figure 16 clearly shows that these guidelines were dramatically exceeded by seasonal mean concentrations in every year since 1975 where data are available.

In summation, fluorine concentrations in both washed and unwashed silver maple foliage have been and continue to be unacceptably elevated.

8 Conclusions

Emissions from the industrial complex occupied by Allied Chemical Canada Ltd. and General Chemical Canada Ltd. in 1987 adversely affected silver maple in the vicinity of the complex. Emissions of fluoride compounds were reflected in elevated foliar concentrations of fluorine in silver maple. The former Control Order, which set a limit for fluorine concentrations in washed silver maple, was exceeded at Station 1 on each sampling date. The consistency with which relatively high or low foliar concentrations were maintained at the sampling stations indicates chronic fumigations by fluoride compounds. However, intermittent peaks in foliar fluorine at some stations indicated acute releases superimposed on the chronic background contamination. Fluoride emissions likely contributed to injury of silver maple foliage. Injury was generally rated as trace in severity.

Emissions of compounds containing sodium were also indicated, although these compounds were not necessarily or exclusively salt (NaCl). The ULN guideline for sodium was regularly exceeded. The variations in sodium concentrations in silver maple foliage indicated episodic exposure to these elements; however, chronic emissions contributed to the elevated concentrations.

Contamination of silver maple foliage by emissions of chlorine was also evident. However, the presence of a second industrial source of chlorine in the geographic area since 1982, and the probability that this source emits chlorine as a gas, precludes ascribing chlorine contamination in the wider Amherstburg area solely to the ACCL/GCCL industrial complex.

While calcium dust releases from the industrial complex occur regularly, foliar calcium concentrations were not excessive and patterns could be ascribed to natural causes. The use of foliage as a monitor of calcium contamination in this case appears to be inappropriate.

A review of historic silver maple foliage chemistry from the permanent sampling stations reveal minor if any long term trends in the concentrations of the contaminants. Sodium concentrations are at or near historic lows; however, historic lows have appeared previously only to be followed by increases in subsequent years. The concentrations have and continue to exceed the ULN guidelines and remain environmentally unacceptable.

Foliar chlorine concentrations were relatively constant from 1979 to 1987 but have had minor year-to-year variations. The 1987 chlorine concentrations are, marginally, the lowest to date. The presence of a second source of chlorine in the Amherstburg area precludes evaluation of the chlorine emission trends from the ACCL/GCCL complex. Chlorine concentrations are still substantially excessive when judged by the Phytotoxicology ULN guidelines.

Fluorine remains the main contaminant of concern with respect to emissions from the industrial complex. Fluorine in washed silver maple foliage has varied from year to year but no trend has been established. The only notable change in fluorine concentrations was a reduction from the very high concentrations of 1975. Fluorine in unwashed foliage has an incomplete record but these concentrations parallel the washed foliage concentrations.

Fluorine concentrations have and continue to be highly excessive relative to the Phytotoxicology Section ULN guideline for unwashed foliage and the former Control Order limit for washed foliage. On the basis of these findings, it is concluded that emission reduction initiatives have not been sufficiently effective to cause a discernable reduction in foliar contamination or to eliminate the potential for injury to vegetation in the area surrounding the ACCL/GCCL industrial complex.

9 Recommendations

The Phytotoxicology Section has been conducting annual surveys in the vicinity of the ACCL/GCCL industrial complex since 1970. Vegetation contamination and injury by industrial emissions have been regularly documented. There has not been any noticeable trend toward emission reductions as reflected by decreases in contaminant concentrations in silver maple foliage. On the basis of these findings, additional action by the Ministry of Environment is warranted to encourage the companies responsible for these emissions to improve their control strategies.

If abatement actions are taken, Phytotoxicology Section monitoring should continue, with the survey being redesigned to improve its capability for ascribing vegetation contamination to the two separate but proximal sources in the Amherstburg area. This would include a new integrated station network with more comprehensive coverage of the area.

While foliage chemistry is a useful medium for detecting contamination by certain types of emissions, it apparently is not useful for detecting calcium contamination in the vicinity of the ACCL/GCCL complex. A network of non-biologic, passive or active monitors would be required to quantify ambient air concentrations of calcium compounds or of specific contaminants such as HCl, HF, Cl₂ or fluorocarbons.

10 References

Bernstein, L., 1980, <u>Salt Tolerance of Fruit Crops</u>, Agriculture Information Bulletin Number 292, United States Department of Agriculture.

Gibson, C., 1988, <u>personal communication</u>, Environmental Officer Technician, Ontario Ministry of the Environment, Windsor District Office.

Linzon, S. N., Chai, B. L. and Hill, A. W., 1973, Fluoride

Studies in the Vicinity of Allied Chemical Hydrofluoric Acid

Plant, Amherstburg, Ontario, 1970 to 1972, Mimeographed

report, Ontario Ministry of the Environment, Air Management

Branch.

Lotus 123, 1986, Lotus 123, Lotus Development Corp., Cambridge, Massachusetts.

Luyt, J. D., 1986, <u>BCM Technologies Ltd.</u>, <u>Amherstburg</u>, Technical Memorandum, Ontario Ministry of the Environment, Southwestern Region.

MOE, 1983, <u>Handbook of Analytical Methods for Environmental Samples</u>, Ontario Ministry of the Environment, Laboratory Services and Applied Research Branch.

NAS, 1971, <u>Fluorides</u>, National Academy of Sciences, Washington, D. C.

Russell, J., 1988, <u>personal communication</u>, Chief Chemist, General Chemical Canada Limited.

SAS, 1979, Statistical Analysis System, SAS Institute Inc., Raleigh, North Carolina.

Phytotoxicology Section Reports
on Vegetation Survey Activities
in the Vicinity of
Allied Chemical Canada Ltd.
and
General Chemical Canada Ltd.,
Amherstburg

Linzon, S. N., Chai, B. L. and Hill, A. W., 1973, Fluoride

Studies in the Vicinity of Allied Chemical Hydrofluoric Acid

Plant, Amherstburg, Ontario, 1970 to 1972, Mimeographed

report, Ontario Ministry of the Environment, Air Management

Branch.

Harper, D., Smith, M. L., Chai, B. and Linzon, S. N., 1974, Investigations of Fluoride Contamination of Vegetation in the Vicinity of Allied Chemical Canada Ltd., Amherstburg, Ontario: May, 1973 to January, 1974, Mimeographed report, Ontario Ministry of the Environment, Air Resources Branch.

Harper, D. S., 1975, <u>Interim Report on the 1974 Regular Surveillance Program in the Vicinity of Allied Chemical Canada Ltd.</u>, <u>Amherstburg</u>, <u>Technical Memorandum</u>, <u>Ontario Ministry of the Environment</u>, <u>Air Resources Branch</u>.

Harper, D. S., 1976, <u>Results of Vegetation Sampling for Control Order Purposes in the Vicinity of Allied Chemical Canada Limited Amherstburg Plant 1975 Growing Season</u>, Mimeographed report, Ontario Ministry of the Environment, Air Resources Branch.

Harper, D. S., 1977, Results of the 1976 Vegetation Sampling Program for Control Order Purposes in the Vicinity of Allied Chemical Canada Ltd., Amherstburg, Mimeographed report, Ontario Ministry of the Environment, Air Resources Branch.

Harper, D. S., 1978, Results of Vegetation Sampling in 1977 in the Vicinity of Allied Chemical Canada Ltd., Amherstburg including the Control Order Sampling Program and Complaint Investigations, Mimeographed report, Ontario Ministry of the Environment, Air Resources Branch.

Cunningham, L. M., 1979, Results of Vegetation Sampling in 1978 in the Vicinity of Allied Chemical Canada Ltd., Amherstburg, Mimeographed report, Ontario Ministry of the Environment, Air Resources Branch.

Harper, D. S., 1980, A Summary of the Results of Vegetation Investigations in the Vicinity of Allied Chemical Canada Limited Amherstburg Plant in 1979, Mimeographed report, Ontario Ministry of the Environment, Air Resources Branch.

Rinne, R. J., 1981, <u>Phytotoxicology Summary Report Allied</u>

<u>Chemical Canada Ltd.</u>, <u>Amherstburg</u>, <u>1980</u>, Mimeographed report,

Ontario Ministry of the Environment, Air Resources Branch.

Vasiloff, G. N., 1983, <u>Phytotoxicology Summary Report Allied</u>
<u>Chemical Canada Ltd.</u>, <u>Amherstburg</u>, <u>1981-1982</u>, Ontario Ministry of the Environment, Air Resources Branch, ARB-93-83-Phyto.

Vasiloff, G. N., 1984, <u>Phytotoxicology Summary Report Allied</u>

<u>Chemical Canada Limited</u>, <u>Amherstburg</u>, <u>1983</u>, Ontario Ministry of the Environment, Air Resources Branch, ARB-94-84-Phyto.

Vasiloff, G. N., 1985, <u>Phytotoxicology Summary Report Allied</u>
<u>Chemical Canada Limited</u>, <u>Amherstburg</u>, <u>1984</u>, Ontario Ministry
of the Environment, Air Resources Branch, ARB-081-85-Phyto.

Vasiloff, G. N., 1986, <u>Phytotoxicology Summary Report Allied Chemical Canada Limited</u>, <u>Amherstburg</u>, 1985, Ontario Ministry of the Environment, Air Resources Branch, ARB-090-86-Phyto.

Vasiloff, G. N., 1988a, Phytotoxicology Summary Report Allied Chemical Canada Limited, Amherstburg, 1986, Ontario Ministry of the Environment, Air Resources Branch, ARB-179-87-Phyto.

Vasiloff, G. N., 1988b, Phytotoxicology Summary Report General Chemical Canada Limited, Amherstburg, 1986, Ontario Ministry of the Environment, Air Resources Branch, ARB-019-87-Phyto.

Summary of Historic Silver Maple Foliage Chemistry
in the Vicinity of
Allied Chemical Canada Ltd.
and

General Chemical Canada Ltd.,

Amherstburg

Stn 1 Stn 16 Stn 18 Stn 29 Stn 30 Stn 31 MONTH SEASON Stn 32 Stn 12 Stn 65

11400 12800

9600 15400

15600 12400

Aug 10400

May

Jun

1982 Jul

		Stn 1	Stn 16	Stn 18	Stn 29	Stn 30	Stn 31	MONTH AVG	SEASON AVG	Stn 32	Stn 12	Stn 65
1983	May Jun Jul Aug Sep	5300 5900 8700 8900 9000	8900 8600 9100 15600 15300	4200 6300 10800 13100 14000	6800 7000 9300 12500 13100	3700 5800 9300 10400 11700	8800 9100 10200 12300 16400	6283 7117 9567 12133 13250	9670	1000 6600 10600 13100 13000	4500 7200 9100 12900 11800	
1984	May Jun	4900 8200 9400 9000 14700	8400 12000 13700 16300 22700	6600 8200 12700 13700 16300	6600 9600 13300 15300 23300	4900 7500 11300 13000 16300	8300 13300 13300 20000 19300	6617 9800 12283 14550 18767	12403	6100 9500 11300 13300 16000	4800 8800 10200 15700 19000	
1985	May Jun Jul Aug Sep	8000 6200 5600 8800 12300	10400 14300 15000 17000 25000	7300 13700 12000 13300 19000	9100 11700 10700 13300 24000	6800 8800 9300 12300 16000	8400 12700 16700 16700 24000	8333 11233 11550 13567 20050	12947	7000 11600 12700 17600 22000	9900 11000 10600 14600 15300	
1986	May Jun Jul Aug Sep	6400 11300 9300 9200 10400	9800 15300 15700 15700 19300	7600 10500 13000 19300 29700	6900 12700 10000 14300 8400	6000 8400 9700 11100 14000	9100 11300 10700 15700 16300	7633 11583 11400 14217 16350	12237	6200 10300 11000 12000 18700	7100 11900 11600 14000 17300	
1987	May Jun Jul Aug Sep	8400 7200 8600 10500 14000	8400 10300 14300 11300 16000	6100 6800 10300 13300 12300	7000 10100 13700 19300 20000	6900 7800 10800 14000 13300	9900 10500 13700 20000 22700	7800 8800 11900 14700 16400	11920	7000 10300 12400 14700 19300	7600 11300 10700 13300 21000	6700 8300 11000 11700 15000

		Stn 1	Stn 16	Stn 18	Stn 29	Stn 30	Stn 31	MONTH AVG	SEASON AVG	Stn 32	Stn 12	Stn 65
SODI	UM (unwashe	d)									
1975	May Jun Jul Aug Sep	not de	termined	i								
1976	May Jun Jul Aug Sep	690 290 300	870 340 380 1000 1830	340 330 620 810 590	310 170 250 430 120	350 110 150 280 240	700 1140 730 2040 270	535 463 403 810 563	555			
1977	May Jun Jul Aug Sep	400 640 1080	840 1930 810 390	490 1250 300 460	290 270 480 210	410 520 520 340	900 1940 8600 740	555 1092 1965 412	1006			
1978	May Jun Jul Aug Sep		ported									
1979	May Jun Jul Aug Sep	240 860 610	5200 1330 450 380 1440	335 380 250 470 1030	290 320 350 430 365	959 680 980 1740 1830	460 2600 2900 2400 1930	1311 925 965 1005 1384	1118			
1980	May Jun Jul Aug Sep	930 265 800		680 253 180 280 255	270 380 470 280 420	380 1170 395 590 480	710 2590 835 900 2440	572 1034 456 575 848	697		163 156 176 106 220	
1981	May Jun Jul Aug Sep	400 190 400	710 350	910 250 217 580 400	271 129 88 173 350	450 350 167 320 200	390 1780 400 1260 1070	630 560 295 514 598	520		160 80 217 80 125	
1982	May Jun Jul Aug Sep	242 163 228	885	440 200 270 244 310	450 137 540 840	310 204 150 218 300	1180 340 440 1300 740	522 224 287 569 521	424		70 67 37 47 265	

		Stn 1	Stn 16	Stn 18	Stn 29	Stn 30	Stn 31	MONTH AVG	SEASON AVG	Stn 32	Stn 12	Stn 65
1983	May Jun Jul Aug Sep	1607 297 270 250 470	657 133 283 440 390	153 83 109 160 497	207 80 130 323 313	320 213 160 170 327	1567 1663 623 1407 1440	752 412 263 458 573	491	463 277 117 127 157	110 50 63 97 93	
1984	May Jun Jul Aug Sep	293 890 1167 687 980	733 450 500 820 1600	200 163 147 200 380	167 110 147 137 237	207 177 573 483 400	1533 2167 867 2733 1433	522 660 567 843 838	686	207 177 250 157 423	120 90 91 81 183	
1985	May Jun Jul Aug Sep	390 403 267 193 390	577 187 293 347 810	377 530 167 170 323	287 99 78 76 333	533 267 307 287 570	397 640 500 507 567	427 354 269 263 499	362	137 156 115 137 253	88 64 55 70 65	
1986	May Jun Jul Aug Sep	227 457 577 197 124	247 167 377 163 320	317 120 137 500 203	123 63 40 113 69	157 193 106 170 243	293 540 233 237 587	227 257 245 230 258	243	120 109 153 72 90	60 93 47 64 84	
1987	May Jun Jul Aug Sep	457 370 620 207 527	187 130 127 393 840	170 127 98 172 150	250 47 120 64 303	507 140 112 147 263	1733 533 327 883 747	551 225 234 311 472	358	110 123 113 73 170	79 74 440 78 92	27 31 26 57 60

								AVG	AVG	
CHLO	RINE	(unwashe	∋d)							
1975	May Jun Jul Aug Sep	not dete	ermined-	-washed	only					
1976	May Jun Jul Aug Sep	not dete	ermined-	-washed	only					
1977	May Jun Jul Aug Sep	not dete	ermined-	-washed	only					ep.
1978	May Jun Jul Aug Sep	not dete	ermined-	-washed	only					
1979	May Jun Jul Aug Sep	0.23 0.32 0.42 0.33 0.67	0.60 0.60 0.45 0.44 0.70	0.12 0.23 0.31 0.33 0.33	0.22 0.41 0.40 0.31 0.43	0.21 0.24 0.26 0.22 0.33	0.15 0.53 0.62 0.47 0.63	0.26 0.39 0.41 0.35 0.52	0.38	
1980	May Jun Jul Aug Sep	0.31 0.24 0.34 0.45 0.43	1.04 0.46 0.39 0.52 0.36	0.41 0.21 0.19 0.29 0.29	0.39 0.29 0.50 0.49 0.29	0.29 0.25 0.20 0.20 0.21	0.36 0.39 0.40 0.52 0.43	0.47 0.31 0.34 0.41 0.33	0.37	0.07 0.07 0.06 0.09 0.09
1981	May Jun Jul Aug Sep	0.26 0.3 0.3 0.4 0.4	0.55 0.5 0.6 0.7 0.2	0.28 0.1 0.6 0.8 0.1	0.27 0.3 0.5 0.5 0.1	0.10 0.1 0.1 0.1 0.1	0.29 0.4 0.5 0.5 0.3	0.29 0.28 0.43 0.50 0.20	0.34	0.11 0.1 0.2 0.2 0.1
1982	May Jun Jul Aug Sep	0.20 0.3 0.4 0.5 0.4	0.34 0.4 1.4 1.0 0.7	0.19 0.2 0.4 0.4	0.26 0.3 0.7 0.6	0.17 0.2 0.5 0.4 0.4	0.36 0.4 0.5 0.8 0.7	0.25 0.30 0.64 0.63 0.58	0.48	0.09 0.1 0.2 0.3 0.5

Stn 1 Stn 16 Stn 18 Stn 29 Stn 30 Stn 31 MONTH SEASON Stn 32 Stn 12 Stn 65

		Stn 1	Stn 16	Stn 18	Stn 29	Stn 30	Stn 31	MONTH AVG	SEASON AVG	Stn 32	Stn 12	Stn 65
1983	May Jun Jul Aug Sep	0.3 0.3 0.3 0.2	0.4 0.3 0.4 0.8 0.8	0.2 0.2 0.3 0.3	0.3 0.3 0.3 0.5	0.2 0.2 0.3 0.4	0.5 0.5 0.5 0.7	0.32 0.30 0.35 0.48 0.53	0.40	0.2 0.1 0.1 0.1 0.2	0.1 0.1 0.2 0.2	
1984	May Jun Jul Aug Sep	0.2 0.3 0.4 0.3 0.5	0.3 0.4 0.5 0.9	0.2 0.2 0.3 0.4 0.5	0.3 0.3 0.4 0.4	0.1 0.2 0.2 0.2 0.3	0.3 0.4 0.4 0.6 0.7	0.23 0.30 0.37 0.47 0.58	0.39	0.1 0.1 0.2 0.2	0.1 0.1 0.1 0.2	
1985	May Jun Jul Aug Sep	0.2 0.2 0.2 0.3 0.4	0.4 0.4 0.8 1.0	0.2 0.4 0.4 0.5	0.3 0.3 0.4 0.4	0.1 0.1 0.1 0.3	0.3 0.5 0.5 0.6	0.25 0.32 0.40 0.52 0.57	0.41	0.1 0.1 0.1 0.2 0.2	0.1 0.1 0.2 0.2	
1986	May Jun Jul Aug Sep	0.2 0.3 0.2 0.3	0.4 0.4 0.5 0.6 0.5	0.3 0.4 0.4 0.7 0.6	0.2 0.2 0.5 0.7	0.1 0.1 0.1 0.1	0.2 0.3 0.2 0.3 0.4	0.23 0.28 0.32 0.45 0.37	0.33	0.1 0.1 0.1 0.1	0.1 0.1 0.2 0.2	
1987	May Jun Jul Aug Sep	0.20 0.23 0.35 0.40 0.04	0.38 0.33 0.40 0.57 0.54	0.17 0.34 0.25 0.35 0.42	0.24 0.21 0.28 0.37 0.49	0.17 0.12 0.08 0.07 0.13	0.34 0.24 0.26 0.39 0.69	0.25 0.25 0.27 0.36 0.39	0.30	0.08 0.10 0.11 0.11 0.16	0.07 0.11 0.13 0.16 0.20	0.11 0.35 0.49 0.47 0.39

		Stn 1	Stn 16	Stn 18	Stn 29	Stn 30	Stn 31	MONTH AVG	SEASON AVG	Stn 32	Stn 12	Stn 6	5
FLUO	RINE	(unwas)	hed)										
1975	May Jun Jul Aug Sep	240 116 240 280 235	99 273 232 287 313	31 50 83 74 85	62 67 572 226 138	58 41 118 79 106	76 102 340 224 200	94 108 264 195 180	168	14 51 191 109 125			
1976	May Jun Jul Aug Sep	87 121 107 274 227	293 51 199 344 225	142 76 102 135 65	54 51 216 343 107	38 25 42 86 33	62 46 56 141 51	113 62 120 221 118	127	75 116 93 93 149			
1977	May Jun Jul Aug Sep	69 35 70 245 141	253 61 106 119 116	216 26 80 90 88	156 77 95 405 107	143 31 52 102 55	263 50 63 138 72	183 47 78 183 97	117	36 16			
1978	May Jun Jul Aug Sep	116 126 562 307	36 97 178 272	11 47 57 89	67 64 130 122	45 77 63 85	68 130 177 74	57 90 195 158	125				
1979	May Jun Jul Aug Sep	32 333 182 362 497	65 102 78 335 468	39 55 81 164 164	26 69 43 107 112	90 82 51 126 94	44 154 190 168 413	49 133 104 210 291	158	12 52			
1980	May Jun Jul Aug Sep	41 134 107 255 325	305 46 37 80 62	127 24 24 83 77	26 112 43 128 88	28 48 19 70 97	255 200 89 255 235	130 94 53 145 147	114		11 14 16 39 42		
1981	May Jun Jul Aug Sep	not rep	ported										
1982	May Jun Jul Aug Sep	not rep	orted										

Stn 1 Stn 16 Stn 18 Stn 29 Stn 30 Stn 31 MONTH SEASON Stn 32 Stn 12 Stn 65 AVG AVG

1983	May Jun Jul Aug Sep	not repor	rted									
1984	May Jun Jul Aug Sep	not repor	rted									
1985	May Jun Jul Aug Sep	not repor	ted									
1986	May Jun Jul Aug Sep	81 180 274 263 250	74 76 39 80 63	70 67 50 116 58	41 57 21 85 18	59 34 28 84 44	82 74 54 91 67	68 81 78 120 83	86	11 56 36 60 57	6 26 21 39 46	
1987	May Jun Jul Aug Sep	346 212 311 203 223	69 33 34 34 67	59 36 29 33 61	29 29 95 27 190	44 19 43 20 58	156 74 86 62 109	117 67 100 63 118	93	44 42 42 24 48	15 13 11 14 32	4 10 8 9 17

		Stn 1	Stn 16	Stn 18	Stn 29	Stn 30	Stn 31	MONTH AVG	SEASON AVG	Stn 32	Stn	12	Stn
FLUO	RINE	(washe	d)										
1975	May Jun Jul Aug Sep	161 116 240 280 235		19 24 39 42 47	79 43 225 125 97	47 32 61 46 66	36 68 187 113 165	66 69 151 129 136	110	14 39 118 76 70			
1976	May Jun Jul Aug Sep	49 75 71 129 141	163 32 39 153 110	78 50 47 59 33	24 34 83 137 59	20 18 16 35 20	42 26 28 66 31	63 39 47 97 66	62	33 51 34 49 60			
1977	May Jun Jul Aug Sep	41 39 42 113 88	84 54 48 49	84 33 35 53 46	85 79 60 126 64	46 32 35 44 40	73 45 44 59 43	69 47 44 74 62	59	17 16			
1978	May Jun Jul Aug Sep	78 64 195 181	18 21 43 157	8 13 25 53	48 29 36 108	23 34 30 62	31 47 48 51	34 35 63 102	58				
1979	May Jun Jul Aug Sep	17 191 144 265 282	14 34 40 156 198	6 21 35 77 98	11 29 32 61 65	51 51 42 63 49	28 95 111 135 168	21 70 67 126 143	86	8 17			
1980	May Jun Jul Aug Sep	15 76 72 143 147	100 22 15 30 28	33 14 14 34 36	12 46 30 84 45	12 28 13 55 53	108 114 45 118 107	47 50 32 77 69	55			5 10 9 22 22	
1981	May Jun Jul Aug Sep	10 85 38 55 76	57 62 46 26 74	9 42 20 50 38	11 40 40 58 48	15 20 10 30 12	15 30 35 26 30	20 47 32 41 46	37			6 10 20 22 14	
1982	May Jun Jul Aug Sep	33 34 50 46 92	14 24 50 62 66	25 17 25 27 33	28 16 41 58 86	29 20 31 24 32	62 58 48 31 74	32 28 41 41 64	41			14 20 11 18 43	

65

		Stn 1	Stn 16	Stn 1	3 Stn	29	Stn	30	Stn 31	MONTH AVG	SEASON AVG	Stn 32	Stn 12	Stn	65
1983	May Jun Jul Aug Sep	15 55 158 86 447	17 17 25 51 117	1 2 5	1 2 5	30 34 49 65 147		9 32 45 76	62 150 89 240 160	26 46 63 90 174	80	3 8 25 39 66	12 5 10 19 26		
1984	May Jun Jul Aug Sep	166 213 .264 138 317	10 20 27 20 38	2 4	7 5)	20 22 38 47 65		11 8 21 15 23	17 55 68 40 72	40 56 74 50 94	63	18 26 41 43 71	10 8 12 14 24		
1985	May Jun Jul Aug Sep	218 100 144 60 225	39 54 59 105 107	3	9 1 9	45 21 51 55 59		24 14 30 18 40	43 45 73 98 60	65 46 64 63 92	66	23 40 32 47 48	7 7 10 15 22		
1986	May Jun Jul Aug Sep	70 98 140 191 270	24 34 20 93 64	1 3 2 11 5	5 3 3	29 25 13 76 16		47 24 19 54 33	53 37 26 50 44	40 42 41 96 80	60	9 31 23 40 49	4 15 13 30 43		
1987	May Jun Jul Aug Sep	194 126 161 153 140	38 24 18 26 46	2 2 1 2: 4	7 3 1	17 21 42 26 75		18 13 14 23 38	61 51 29 44 60	60 44 47 49 68	53	32 35 28 27 43	8 9 9 13 27		3 8 4 11 14

